Supporting information for "Self-assembly of multicomponent structures in and out of equilibrium'

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MOTIVATION OF ANALYTIC THEORY

The analytic theory developed in the main text is a dynamical mean-field one, which focuses on the likelihood $\phi \equiv [(\eta_i + 1)/2]$ that a given fiber bond is a bulk one. Here $\eta_i \equiv S_i S_{i+1}$, is a 'defect variable': $\eta_i = 1$ describes a bulk (same-color) bond, and $\eta_i = -1$ is a defect (unlike-color) one. We expect a mean-field theory of this nature to be most accurate when red and blue blocks are added to the fiber with equal likelihood, because, in this limit, the Ising model representation of fiber energetics can be written in the noninteracting (space-independent) form $\mathcal{H} = -J \sum_i \eta_i$.

To derive Eqns. (1) and (2) of the main text, we argue as follows. At any instant, the end of the fiber is either red or blue. Regardless, the next block added is of matching color with probability 1/2, and so we expect bulk domains to grow with rate $c/2$. We expect bulk domains to shrink with rate $\phi \mathrm{e}^{-\beta\epsilon_\mathrm{s}}$: the factor ϕ ensures that the terminal bond is a bulk one, and the factor $\mathrm{e}^{-\beta\epsilon_\mathrm{s}}$ contains the energy scale for the bulk interaction. Similarly, we expect the fiber as a whole to grow with rate c, and to shrink with rate $\mathrm{e}^{-\beta\epsilon_\mathrm{s}}$ (resp. $\mathrm{e}^{-\beta\epsilon_\mathrm{d}}$) if its rightmost bond is a bulk (resp. defect) one. These arguments imply the drift velocities for bulk domains and for the fiber given in Eqns. (1) and (2) of the main text.

DYNAMIC CORRELATION LENGTH

The dynamic correlation length ξ derived from Eq. (3) of the main text is

$$\xi(c, \epsilon_\mathrm{s}, \epsilon_\mathrm{d}) = \frac{2(\mathrm{e}^{\beta\epsilon_\mathrm{s}} - \mathrm{e}^{\beta\epsilon_\mathrm{d}})}{\mathrm{e}^{\beta\epsilon_\mathrm{s}} + \mathrm{e}^{\beta\epsilon_\mathrm{d}}(c\,\mathrm{e}^{\beta\epsilon_\mathrm{s}} - 1) - \sqrt{(\mathrm{e}^{\beta\epsilon_\mathrm{d}} - \mathrm{e}^{\beta\epsilon_\mathrm{s}})^2 + c^2\mathrm{e}^{2\beta(\epsilon_\mathrm{s}+\epsilon_\mathrm{d})}}} \tag{S1}$$

when $\epsilon_\mathrm{s} \neq \epsilon_\mathrm{d}$, and $\xi = 2$ otherwise.

SUPPLEMENTAL FIGURES

Figs. S1– S4 supplement Fig. 1 of the main text; Fig. S5 supplements Fig. 2 of the main text.

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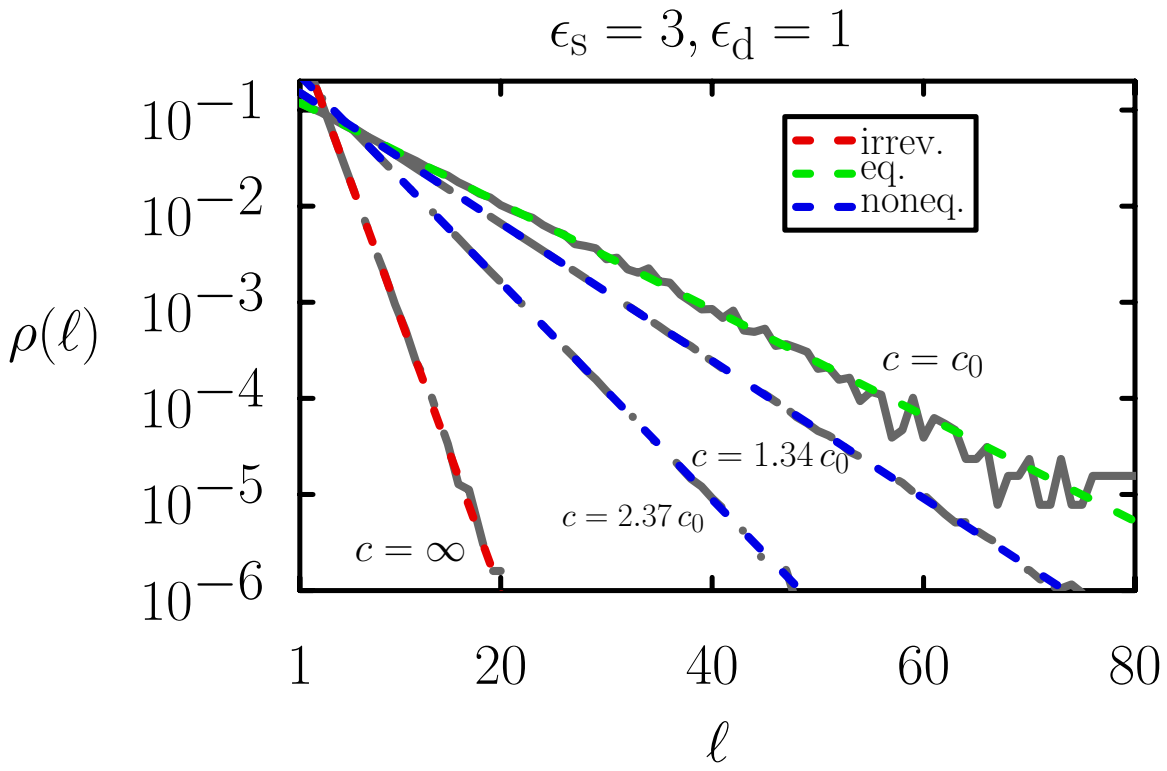

FIG. S1: Dynamic fiber domain length distributions are exponential. We show $\rho(\ell)$ obtained from simulations (grey lines), for selected concentrations at and past the phase boundary $c = c_0$, for a set of conditions considered in Fig. 1 of the main text. Overlaid are analytic estimates of the domain length distribution, $\rho(\ell) = (\xi - 1)^{-1} \exp\left[\ell \ln(1 - \xi^{-1})\right]$, where the mean domain length ξ is obtained from self-consistent mean field theory (Eq. (S1)) (blue). When $c = c_0$ this reduces to the equilibrium value $\xi_0 = 1 + \exp(\beta(\epsilon_s - \epsilon_d))$ (green); when $c \to \infty$ we obtain the random adsorption limit $\xi_\infty = 2$. In all cases the analytic expressions match the simulation results. Because observed domain length distributions are exponential, we consider only the mean domain length ξ in Fig. 1 of the main text.

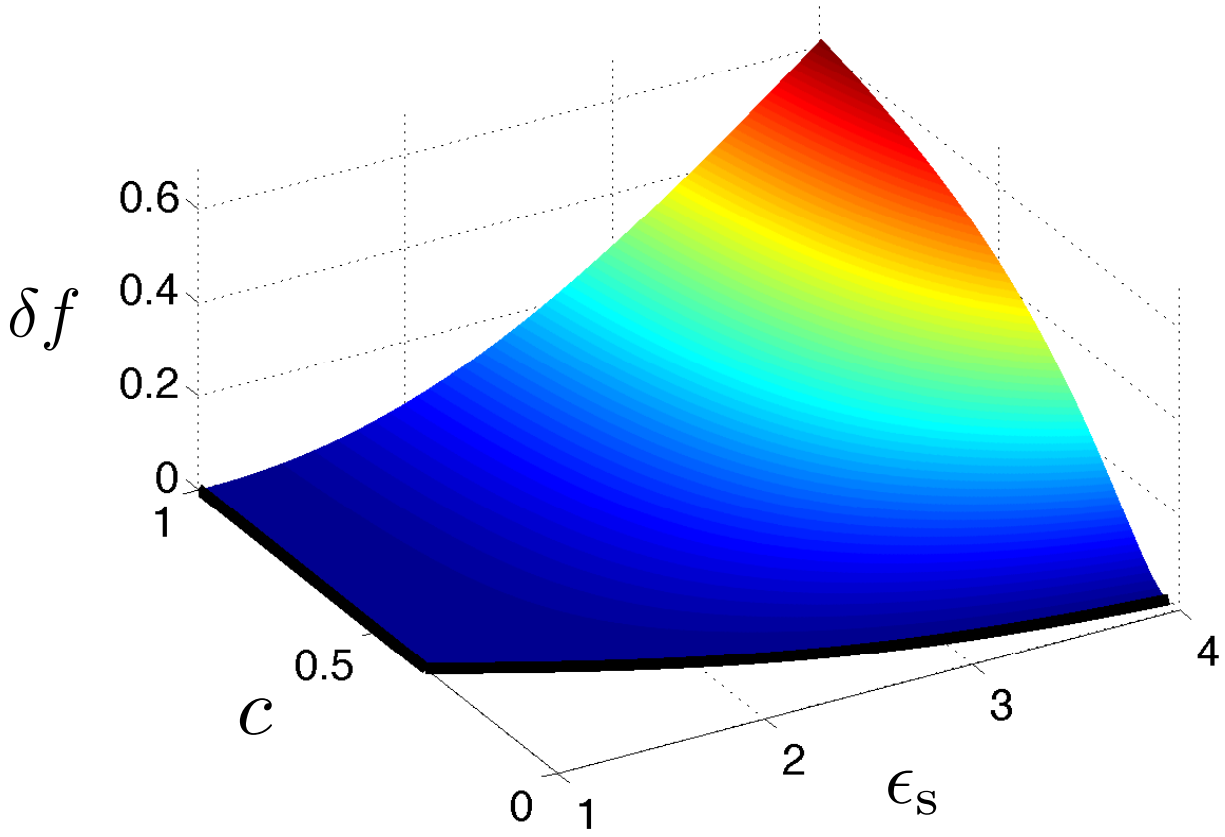

FIG. S2: Excess free energy $\delta f \equiv f(\phi) - f(\phi_0)$ per fiber block as a function of concentration c and like-color energy scale ϵ_s (note that $\epsilon_d = 1$). Here ϕ_0 is the equilibrium bulk fiber fraction, and ϕ is its dynamic counterpart, here computed using Eq. (3) of the main text. The free energy is $f(\phi) = (\epsilon_s - \epsilon_d)(1-\phi) + k_B T\,(\phi \ln \phi + (1-\phi)\ln(1-\phi))$; at all points past the phase boundary, dynamically-generated structures lie higher in free energy than equilibrium ones. An exception occurs when $\epsilon_s = \epsilon_d$, because there the compositional correlations of the equilibrium structure are equal to those of random mixing.

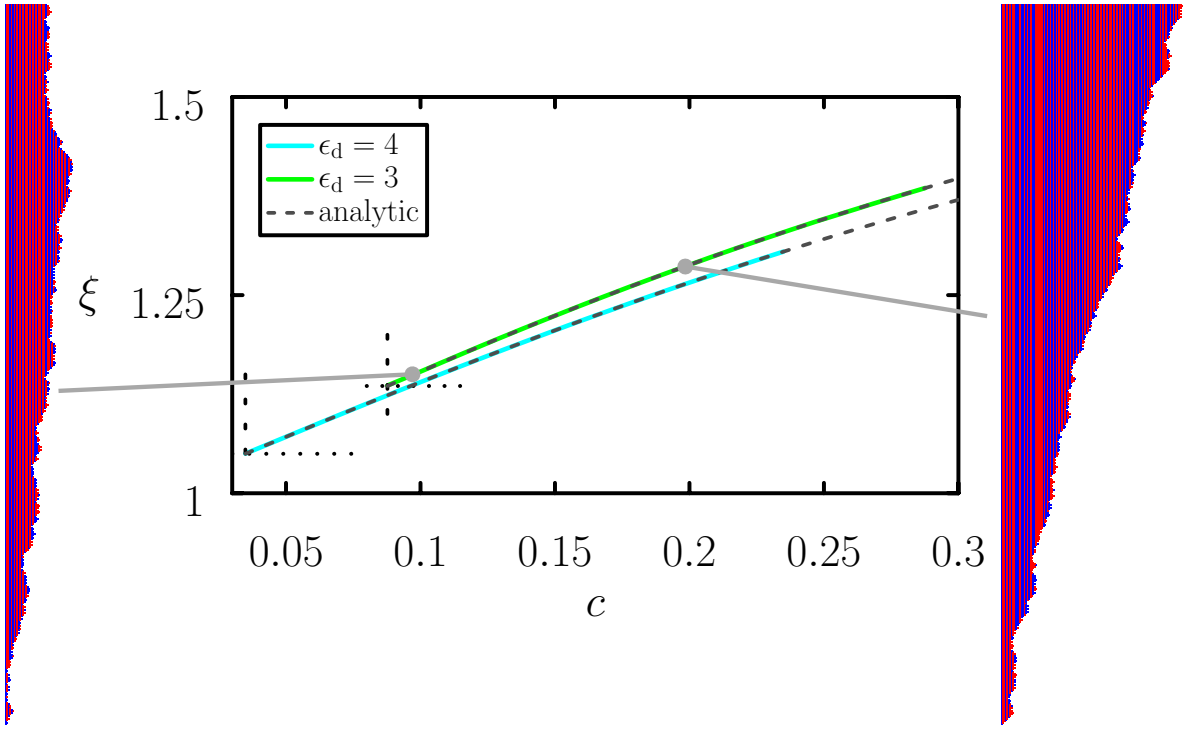

FIG. S3: As Fig. 1 of main text, but for the case $\epsilon_d > \epsilon_s$ (here $\epsilon_s = 1$), giving an effective Ising antiferromagnetic coupling $J = (\epsilon_s - \epsilon_d)/2 < 0$. In this case the equilibrium structure mimics that of a binary crystal, consisting (in the limit of large ϵ_d) of alternating blue and red blocks. We observe the same breakdown of the quasiequilibrium assumption as for the case $J > 0$ (phase boundaries and equilibrium correlation lengths are labeled in the same manner). However, because the numerical difference between the domain length associated with random mixing ($\xi_\infty = 2$) and equilibrium ($\xi \to 1$ for large ϵ_d) is small, structures grown close to the phase boundary are numerically similar to their equilibrium counterparts.

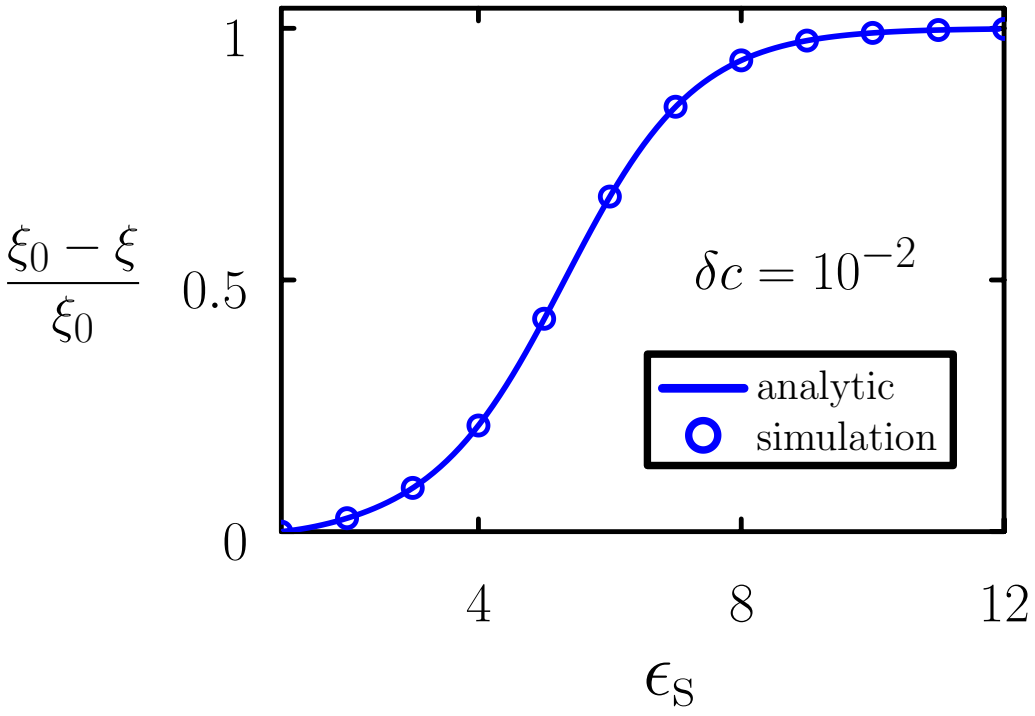

FIG. S4: For fixed absolute supersaturation $\delta c \equiv c - c_0$, the 'distance' $(\xi_0 - \xi)/\xi_0$ from equilibrium of dynamically generated fiber structures grows sharply with increasing energy scale ϵ_s. Here $\epsilon_d = 1$.

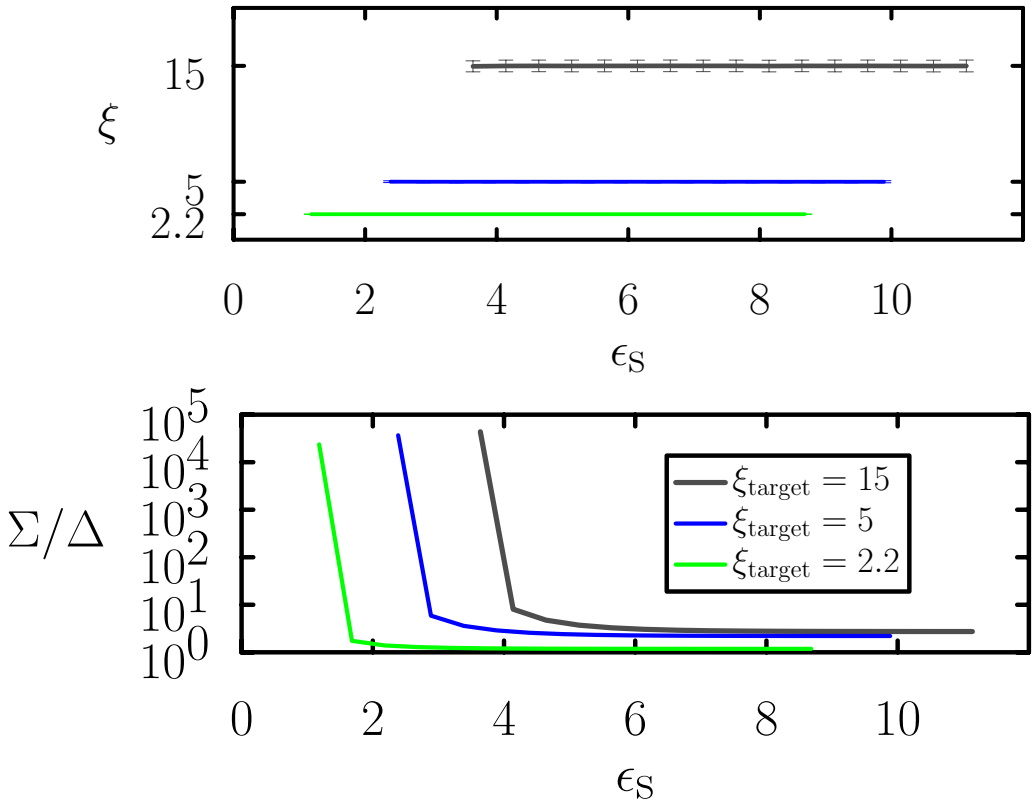

FIG. S5: Simulations performed at the locations specified by the circles in Fig. 2, main text, bear out the analytic prediction that identical structures are generated along contours (top panel), by growth protocols displaying markedly different degrees of microscopic reversibility (bottom panel). $\Sigma \equiv N_+ + N_-$ is the total number of binding (N_+) and unbinding (N_-) events taking place during the assembly of fibers of length $L = 2.5 \times 10^4$ blocks ($\Delta \equiv N_+ - N_- = L$ is the net number of binding events). At the phase boundary, fibers grow only diffusively. As a result, $\sim L^2$ microscopic events are required to generate a structure of length L. Far from the phase boundary, assembly is much less reversible.